

Molecular Dynamics Computer Simulation of the Dynamics of Supercooled Silica

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We present the results of a large scale computer simulation of supercooled silica. We find that at high temperatures the diffusion constants show a non-Arrhenius temperature dependence whereas at low temperature this dependence is also compatible with an Arrhenius law. We demonstrate that at low temperatures the intermediate scattering function shows a two-step relaxation behavior and that it obeys the time temperature superposition principle. We also discuss the wave-vector dependence of the nonergodicity parameter and the time and temperature dependence of the non-Gaussian parameter.

1 Introduction

In the last few years ample evidence was given that computer simulations are a very useful method to study the dynamics of supercooled liquids (Barrat and Klein 1991, Yip 1995, Kob 1995, Paul and Baschnagel 1995). Apart from some rare exceptions, such as, e.g., the recent simulation of supercooled water by Sciortino *et al.* (Gallo *et al.* 1996, Sciortino *et al.* 1996), most of these simulations were done for liquids for which the *local* structure is similar to the one of a closed packed hard sphere system. Thus the dynamics of systems in which the particles form an open network structure, such as SiO₂ or B₂O₃, has hardly been investigated with computer simulations at all, although there is a large body of experiments in which such materials have been studied (see, e.g., the papers in Ngai 1994). In this paper we present some of the results of a large scale molecular dynamics computer simulation in which we investigated the dynamics of SiO₂ in its supercooled state.

2 Model

The model we use to describe silica is given by the potential proposed a few years ago by van Beest *et al.* (van Beest, Kramer and van Santen 1990), and is of the form

$$\phi(r_{ij}) = \frac{q_i q_j e^2}{r_{ij}} + A_{ij} e^{-B_{ij} r_{ij}} - \frac{C_{ij}}{r_{ij}^6} \quad . \quad (1)$$

The values of the various parameters can be found in the original publication. This potential has been shown to give a correct description of the different crystalline phases of silica (Tse and Klug 1991; Tse, Klug and Allan 1995) and in a recent publication Vollmayr *et al.* (Vollmayr, Kob and Binder 1996) have shown that it

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is also able to reproduce many static properties of amorphous silica and that this system forms a network of tetrahedra, each of which has a silicon atom in its center and which are interconnected by bridging oxygen atoms. Thus we conclude that this model gives a quite realistic description of this network glassformer. Note that in the simulation of Vollmayr *et al.* the non-Coulombic interactions were truncated and shifted at a distance of 5.5\AA and in the present work we have done so likewise.

The simulations were done at constant volume and the density of the system was fixed to 2.3 g/cm^3 . In order to avoid finite size effect in the dynamics (Horbach, Kob, Binder and Angell 1996), the size of the system was relatively large and consisted of 8016 ions. The equations of motion were integrated with the velocity form of the Verlet algorithm and the Coulombic contributions to the potential were calculated with the Ewald summation. The time step of the integration was 1.6 fs and the longest runs were $4 \cdot 10^6$ time steps, thus 6.4 ns. At each temperature the system was equilibrated with a stochastic heat bath for a time which was at least as long as the subsequent production run. The temperatures investigated were 6100 K, 5200 K, 4700 K, 4300 K, 4000 K, 3900 K, 3760 K, 3580 K, 3400 K, 3250 K, 3100 K, 3000 K and 2900 K, the lowest temperature at which the system could be equilibrated within the time span of our simulation. More details on the simulation will be given elsewhere (Horbach and Kob 1997).

3 Results

One of the simplest quantities to describe the dynamics of the system is the tracer diffusion constant D which can be computed from the mean square displacement of a tagged particle. In Fig. 1 we show D for the silicon and oxygen atoms in an Arrhenius plot. We recognize that at high and intermediate temperatures the diffusion constants clearly show a deviation from the Arrhenius behavior which is found experimentally, although at lower temperatures than we investigated (Brébec *et al.* 1980, Mikkelsen 1984). However, at the lowest temperature considered here, our data is also compatible with an Arrhenius temperature dependence (bold solid lines). The activation energies obtained here, 4.45 eV for O and 4.9 eV for Si, are in surprisingly good agreement with the experimental values (4.7 eV for O (Mikkelsen 1984) and 6 eV for Si (Brébec *et al.* 1980)).

Motivated by the proposition of the so-called mode-coupling theory (MCT) (Götze 1991, Götze and Sjögren 1992), we also attempted to fit our data for intermediate and low temperatures with a power-law, i.e. $D \propto (T - T_c)^\gamma$. The result of this fit is included in the figure as well (thin solid lines) and we recognize that this functional form is able to describe the data very well. Note that the critical temperature $T_c = 2260\text{ K}$ is the same for both types of atoms. (As one might have expected, for strong glass formers, T_c is well above the experimental glass transition temperature $T_g \approx 1450\text{ K}$). Hence we can infer that at our lowest temperatures the diffusion constants make a crossover from a power-law behavior to an Arrhenius behavior. Thus from our simulation we can make the conjecture that at high enough temperatures *real* silica will make a transition from being a strong glass former (Angell 1985), which shows an Arrhenius temperature dependence of the transport coefficients, to a fragile glass former, which shows a power-law like temperature dependence. This prediction is also in agreement with recent

propositions of Rössler and Sokolov (Rössler and Sokolov 1996).

In Fig. 2 we show the time dependence of the incoherent intermediate scattering function $F_s(q, t)$ for silicon for all temperatures investigated. The wave-vector is 1.7 \AA^{-1} , the location of the first sharp diffraction peak in the structure factor. We see, Fig. 2a, that even at relatively high temperatures $F_s(q, t)$ shows a shoulder at around 0.6 ps, which develops into a plateau upon further cooling. Thus we find that also this network glassformer shows the typical two-step relaxation behavior that is known for fragile glasses and whose existence is one of the predictions of MCT. For the lowest temperatures we also observe that the correlation function shows a dip around 0.2 ps. This feature is likely related to the so-called boson peak, which has also been observed in n-scattering experiments of vitreous silica (Buchenau *et al.* 1986).

We define the α -relaxation time $\tau(T)$ as the time it takes the correlation function to decay to e^{-1} of its initial value. MCT predicts that if a time correlation function is plotted versus the rescaled time $t/\tau(T)$, one obtains a master curve [time-temperature superposition principle (TTSP)]. That this is indeed the case is demonstrated in Fig. 2b, where we show the same curves as in Fig. 2a, but versus $t/\tau(T)$. For rescaled times $t/\tau \geq 1$, i.e. in the α -relaxation regime, the curves for the different temperatures fall nicely on top of each other, thus showing that in this time regime the TTSP holds. This is not *quite* the case for $t/\tau \leq 1$, i.e. in the β -relaxation region. However, a closer inspection of the individual curves shows that the reason for the lack of a perfect scaling is likely the fact that the curves show the aforementioned dip at early times. At the very lowest temperatures, the location of this dip has been moved to such small rescaled times, that the scaling of the curves works very well again. Thus we find that at low enough temperatures the TTSP works also in the β -relaxation regime. Similar conclusions hold also for other wave-vectors and the oxygen atoms (Horbach and Kob 1997).

The intermediate scattering function can be measured *relatively* easily in scattering experiments. This is not the case for the so-called non-Gaussian parameters $\alpha_i(t)$, which are a measure for how strongly $F_s(q, t)$ deviates from a Gaussian behavior (Rahman 1964), whereas these functions can be calculated easily in a computer simulation. (In recent n-scattering experiments by Buchenau *et al.* and Zorn the time dependence of α_2 was determined (Buchenau *et al.* 1996, Zorn 1996)). In Fig. 3 we show the time dependence of $\alpha_2 = 3\langle r^4(t) \rangle / 5\langle r^2(t) \rangle^2 - 1$ and $\alpha_3 = 3\langle r^6(t) \rangle / 35\langle r^2(t) \rangle^3 - 1$ for the oxygen atoms, where $r(t)$ is the probability that a tagged particle travels a distance r in time t .

From this figure we see that for short times α_i is zero, as it should be, and then starts to increase when the system enters the β -relaxation region. After having reached a maximum value at a time which corresponds to approximately the end of the β -relaxation regime, the curves start to drop back to zero. The height of this maximum increases with decreasing temperature, thus showing that the Gaussian approximation breaks down more and more the lower the temperature is. It is also interesting that for very short times, ≈ 0.04 ps, $\alpha_{1/2}$ show a small peak. A similar peak was also found in a computer simulation of a Lennard-Jones system (Kob and Andersen 1995a), although with much smaller amplitude. Since this latter system is not a network forming glass and quite fragile, we conclude that this feature is probably not closely connected to the details of the structure of the system but is more likely a feature that is related to the dynamics of supercooled

liquids.

The last quantity we investigate is the wave-vector dependence of the nonergodicity parameter, i.e. the height of the plateau in a time correlation function at low temperatures (Götze 1991, Götze and Sjögren 1992). For the case of the coherent and incoherent intermediate scattering function this is thus nothing else than the Debye-Waller and Lamb-Mössbauer factor, respectively. In Fig. 4 we show the nonergodicity parameters $f_c^{(s)}(q)$ and $f_c(q)$ for the incoherent scattering function of the silicon atoms and the coherent scattering function for the silicon-silicon correlation, respectively. We see that $f_c^{(s)}$ shows a Gaussian like dependence on q , as it has already been observed for the case of simple liquids (Kob and Andersen 1995b), and is also predicted by MCT. The nonergodicity parameter for the coherent scattering function shows several maxima and minima, the location of which are the same as the ones observed in the structure factor. Also this observation is in qualitative agreement with the one made for simple liquids and the prediction of MCT. It is also interesting to note that at a wave-vector of approximately 8\AA^{-1} the nonergodicity parameters have decayed to essentially zero, whereas the three partial structure factors show a significant wave-vector dependence even for larger values of q . This is in contrast to what has been found in the case of simple liquids (Kob and Andersen 1995b), where the value of the wave-vector at which the nonergodicity parameters become zero and the ones at which the partial structure factors become constant are almost identical. It would be interesting to understand whether this observation is just a particularity of silica or whether it is a general property of network forming glasses.

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Figures

Figure 1: Arrhenius plot of the diffusion constant for the silicon atoms (filled squares) and oxygen atoms (open circles). Thin solid lines: Fit with a power-law. Bold solid lines: Fit with an Arrhenius-law.

Figure 2: Incoherent intermediate scattering function for the silicon atoms vs. time (a) and rescaled time (b) for all temperatures investigated.

Figure 3: Time dependence of the non-Gaussian parameters α_2 (a) and α_3 (b) for all temperatures investigated (main figure). Inset: Same data at short times.

Figure 4: Wave-vector dependence of the nonergodicity parameter for the incoherent scattering function of the silicon atoms (open circles) and of the coherent scattering function of the silicon-silicon correlation (filled squares).











